ACS Standard Physical Chem Exam Taken Yesterday by 15 students

	Score(out of 60)	Percent
	30	50.0
	29	48.3
	28	46.7
	27	45.0
	27	45.0
	26	43.3
	25	41.7
	24	40.0
	23	38.3
	22	36.7
	21	35.0
	18	30.0
	17	28.3
	15	25.0
	15	25.0
average	**23.1**	**38.6%**
361 last year		**43%**
National Average =		**52%**

CHMY 361 How to ***estimate*** your final grade **Handout #13**

December 5, 2016

Total points = 700; Homework is worth 100; midterms = 100 each, and final =200

The total possible homework points =143, so:

Total % = (total HW/143 * 100 + total exam points)/700

Last year's letter grades were typical, but could be slightly different this year.

Total %	Grade
90-100	A
86-89	A-
80-85	B+
75-80	B
70-74	B-
68-70	C+
63-67	C
60-62	C-
50-59	D

LE CHATLIER'S PRINCIPLE

A SYSTEM AT EQUILIBLIUM WILL REACT TO CHANGES ("Stresses") THAT DESTROY THE EQUILIBRIUM, SO AS TO RELIEVE THE STRESS

NOT pure solid or liquid

1. Increased Concentrations WILL be REDUCED *

Decreased Concentrations WILL be INCREASED *

$\Delta H \neq 0$ React.

2. Heat added will be USED *
" removed " " REPLACED *

$\Delta V \neq 0$ React.

3. Pressure applied Causes Volume DECREASE *
" decrease " " INCREASE *

* IF THE SYSTEM IS ABLE TO

For *ideal* gases and solutions

$n_A A + n_B B + \rightarrow n_C C + n_D D$

$$\Delta G_r = +\Delta G_r^0 - RT\ln(C_A/C^0_A)^{n_A} - RT\ln(C_B/C^0_B)^{n_B} + RT\ln(C_C/C^0_C)^{n_C} + RT\ln(C_D/C^0_D)^{n_D}$$

which says increasing ***reactant*** conc. makes ΔG_r more negative (shifts reaction to right)

which says increasing ***product*** conc. makes ΔG_r more positive (shifts reaction to left)

$$\Delta G_r = \Delta G_r^0 + RT\ln(Q/Q^0), \text{ where:}$$

$$Q = \frac{C_C^{n_C} C_D^{n_D}}{C_A^{n_A} C_B^{n_B}}$$

$$Q^0 = \frac{\left(C_C^0\right)^{n_C}\left(C_D^0\right)^{n_D}}{\left(C_A^0\right)^{n_A}\left(C_B^0\right)^{n_B}}$$

Q^0 is always 1:
1 bar, 1 molar, or X (molefraction) = 1 (pure liquid or solid)

except for the biochemical standard state where $C(H^+) = 10^{-7}$

At ***equilibrium***:

$$\Delta G_r = \Delta G_r^0 + RT\ln(Q_{equil}/ Q^0) = 0$$

Therefore: $\Delta G_r^0 = -RT\ln(K/ Q^0)$

$\Delta G^0 = -RT\ln (Q_{eq}/Q_0) = -2.3RT\log K$

at 25^0C $2.3RT = 2.3 \times 8.3145 \times 298 = 5.7$

$\Delta G^0 = -2.3RT\log (Q_{eq}/Q_0) = -5.7\log (K)$

K = ?

$$K = 10^{-\frac{\Delta G^0}{2.303RT}} = 10^{-\frac{\Delta G^0}{5.7}}$$

ΔG^0 kJ/mol	K
17.1	0.001
11.4	0.01
5.7	0.1
0	1
-5.7	10
-11.4	100
-17.1	1000

1. Equilibrium constant, K, is just a Boltzmann Distribution

At constant T and V and no work :

$\Delta A^0 < 0$ **means the process is spontaneous**

and $K = e^{\frac{-\Delta A^0}{RT}} = e^{\frac{-(\Delta U^0 - T\Delta S^0)}{RT}} = e^{\frac{\Delta S^0}{R}} e^{\frac{-\Delta U^0}{RT}}$ **, if J/mol units**

$= e^{\frac{\Delta S^0}{k_B}} e^{\frac{-\Delta U^0}{k_B T}}$ **, if J/molcule units, where** $\mathbf{k_B}$ **= R/6x10**^{23}

$$= \frac{g_{prod}}{g_{react}} e^{\frac{-\Delta U^0}{k_B T}}$$

$$K = \frac{g_{prod}}{g_{react}} e^{\frac{-(U^0_{prod} - U^0_{react})}{k_B T}}$$

(20 pts) **3.** The wavelength of maximum emission of electromagnetic radiation from an object that is at the average temperature of the surface of the sun (T=5600K) is 500 nm (green light). **Question:** What is the ratio of the number of molecules in the energy level that emits 500 nm radiation to the number of molecules in the ground state at 5600 K if the number of available states in the upper level is 1000 times that for the ground state? with $k_B = 0.697\ cm^{-1}$

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} e^{-\frac{\Delta E}{KT}}$$

$$\frac{1}{500 \times 10^{-9}\ m \times \frac{10^2\ cm}{m}} = 20\,000\ cm^{-1}$$

$$= 1000\ e^{\frac{-20000}{(0.697)(5600)}} = 5.95$$

What if $\Delta E = 20{,}000\ J\ mol^{-1}$?

$N_2/N_1 = 1000 \times \exp(-20000\ J\ mol^{-1}/(8.3145\ J\ mol^{-1}\ K^{-1} \times 5600\ K))$

Standard States

Gases: 1 atm partial pressure (new convention is 1 bar) and ***ideal.****

Liquids and Solids: 1 atm and pure ($x = 1$, where x is the mole fraction of the liquid.

Solutes: 1 molar (sometimes 1 molal or $x_{solute} = 1$) and ***ideal.*****

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* The enthalpy is as if the gas is at such a low pressure that it behaves ideally, but the entropy is as if it is at 1 atm.

** The enthalpy is as if the solute concentration is so low that the solution is ideal (no significant solute-solute interactions) but the entropy corresponds to unit concentration.

THE REAL Q

recall: $\Delta G = \Delta G^\circ + RT \ln\left(\frac{Q}{Q^\circ}\right)$ always

FOR IDEAL gases & solutions:

the reaction $n_A A + n_B B \rightarrow n_C C + n_D D$

$$Q_{Ideal} = \frac{C_C^{n_C} C_D^{n_D}}{C_A^{n_A} C_B^{n_B}}$$

γ = activity coef.

γC = activity = a

$$Q_{real} = \frac{a_C^{n_C} a_D^{n_D}}{a_A^{n_A} a_B^{n_B}} = \frac{(\gamma_C C_C)^{n_C} (\gamma_D C_D)^{n_D}}{(\gamma_A C_A^{n_A})(\gamma_B C_B^{n_B})}$$

Note ERROR
In denominator!

If $\gamma_A < 1$ $\bar{G}_A$ i.e., μ_A is more neg.
than expected from Conc.
i.e. more stable

If $\gamma_A > 1$ μ_A is less stable

STANDARD STATE: $C = 1$ $\gamma = 1$

so $Q^\circ = 1$ (in this course.)

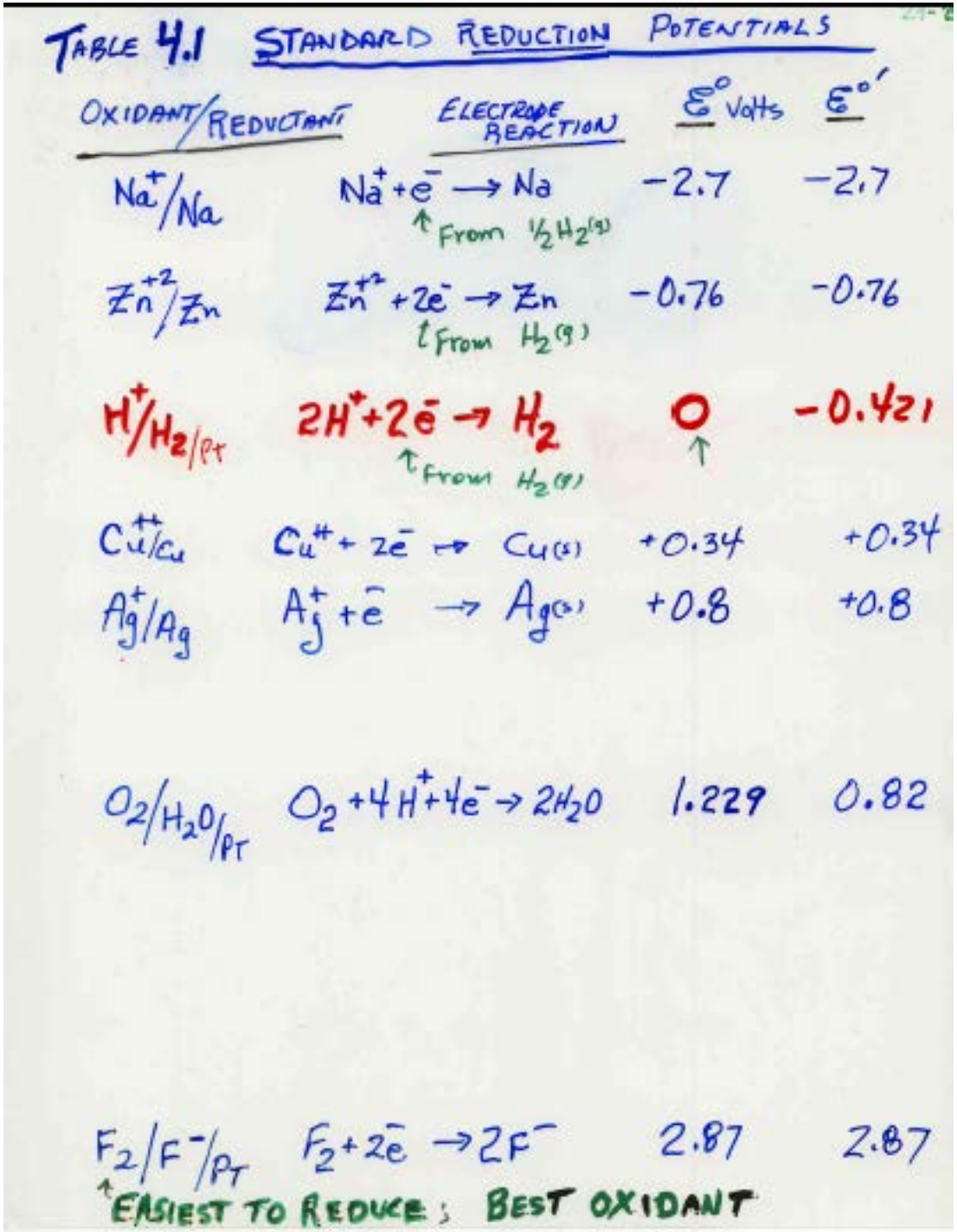


TABLE 4.1 STANDARD REDUCTION POTENTIALS

OXIDANT/REDUCTANT	ELECTRODE REACTION	$\mathcal{E}^\circ$ Volts	$\mathcal{E}^{\circ\prime}$
Na^+/Na	$Na^+ + e^- \rightarrow Na$ (↑ From $\frac{1}{2}H_{2(g)}$)	−2.7	−2.7
Zn^{+2}/Zn	$Zn^{+2} + 2e^- \rightarrow Zn$ (↑ From $H_{2(g)}$)	−0.76	−0.76
$H^+/H_{2/Pt}$	$2H^+ + 2e^- \rightarrow H_2$ (↑ From $H_{2(g)}$)	0 ↑	−0.421
Cu^{++}/Cu	$Cu^{++} + 2e^- \rightarrow Cu_{(s)}$	+0.34	+0.34
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag_{(s)}$	+0.8	+0.8
$O_2/H_2O/_{Pt}$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229	0.82
$F_2/F^-/_{Pt}$	$F_2 + 2e^- \rightarrow 2F^-$	2.87	2.87

↑ EASIEST TO REDUCE; BEST OXIDANT

$$\Delta G^0 = -nF\xi^0$$

volts = J/coulomb

intensive (like temperature).

independent of moles

(20 pts) **8.** Given the following information from a table of reduction potentials:

$A^{2+} + 2e^- \text{ ---> } A$ $\quad E^0 = -0.4$ volts final

$B^+ + 1e^- \text{ ---> } B$ $\quad E^0 = +0.7$ volts init

(a) What is the standard cell potential for the conversion of A^{2+} to A by reaction with B? $B + A^{2+} \longrightarrow B^+ + A$

electrons start on B, end on A

$$\mathcal{E}^0_{cell} = \mathcal{E}^0_{final} - \mathcal{E}^0_{init} = -0.4 - (0.7) = \boxed{-1.1 \text{ volts}}$$

(b) What is ΔG^0 for the process in (a) that produces 2 moles of A?

$n_e = 2 \times 2 = 4$ mols e^-

$$\Delta G^0 = -nF\mathcal{E}^0 = -4 \times 96{,}500 \text{ Coul} \times +1.1 \frac{J}{\text{Coul}}$$

$$= \boxed{+424500 \text{ J}}$$

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a \equiv K_d = \frac{[H^+] \cdot [A^-]}{[HA]}$$

If $[H^+] = K_d$ $[A^-] = [HA]$

50% protonated. (Bound)

i.e. 50% dissociated

PT $\rightleftharpoons$ P + T

$$K_d = \frac{[P]\,[T]}{[PT]}$$

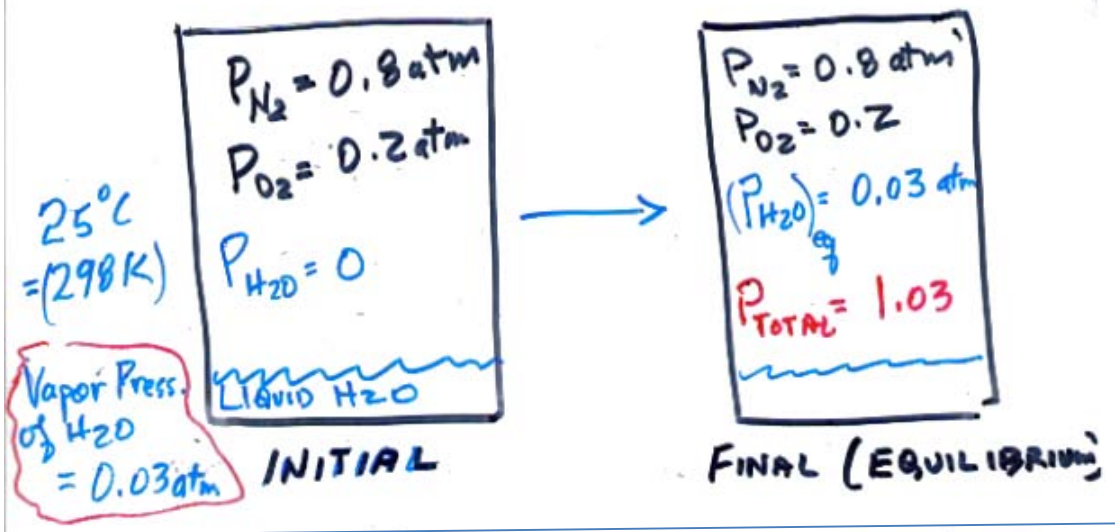
when $[P] = K_d$ 50% Bound.

If $K_d = 1 \times 10^{-9}$ M $= 1$ nm

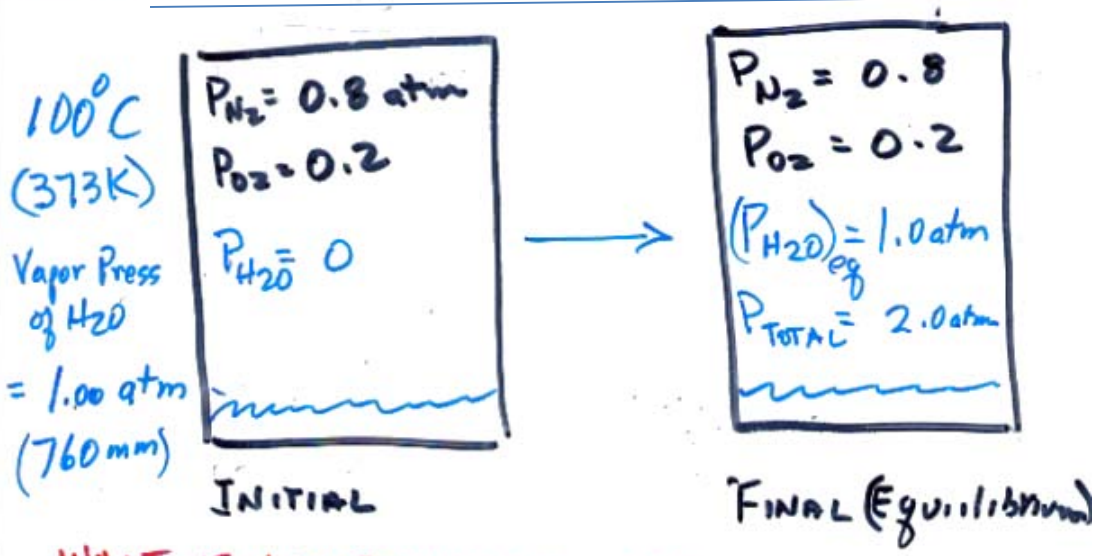
"P binds at the nm level"

09 5-2

More Partial Pressure & "Vapor Pressure"



25° C



100° C

WHAT IF WE REDUCE THE SPACE BY 50% ?

$P_{N_2} = ?$ 1.6 $P_{O_2} = ?$ 0.4 $P_{H_2O} = ?$ 1.00

20 pts) **1.** (12 pts) If an isothermal, constant volume spontaneous process clearly creates a final state that is more ordered than the initial state, and if P = Pext = constant, and there is PV work only, tell whether the following are positive, 0, or negative . Indicate your reasoning very briefly.

$\Delta H = q$

q __−__ w __0__ ΔE __−__ ΔH __−__ ΔS __−__ ΔG __−__

$\Delta G < 0$ spontaneous. $\Delta G = \Delta H - T\Delta S$ (− ↑ +)

$\Delta S < 0$ ordering.

$w = 0$ $\Delta V = 0$ $w = -P_{ex}\Delta V$

$\Delta E = q + w = -$ ($w \to 0$)

(15 pts) 3. Supercooled (much below freezing point) water suddenly turns to ice in an ***isolated*** chamber at constant pressure, and eventually comes to equilibrium. Tell whether the following are positive, zero, or negative. Give a brief justification for each of your answers. If it is not possible to unequivocally know the answer for any of these, indicate this and say why.

q 0 w 0 ΔT + ΔU 0 ΔH ? * see below * ΔS + ΔG ? ΔS_{surr} 0 ΔS_{univ} +

q, w, ΔU = 0 because isolated

ΔT = + exothermic & isolated.

ΔS = ΔS_{univ} = + it happened and isolated

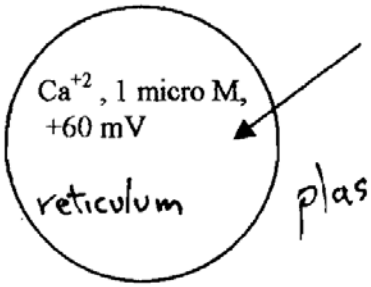
ΔS_{surr} = 0 isolated

ΔH = ΔU + Δ(PV) = 0 + what you assume for ΔPV

ΔG = ΔH − TΔS = ? if you make no assumption about ΔPV or if ΔPV = neg.

= negative if you assume ΔPV = 0

(20pts) **7. (a)** Calculate the ΔG for transferring 0.5 mole of Ca^{+2} into the endoplasmic reticulum from the plasma (outside) if the potential is 60 mV more positive inside and the concentration is 1 nano M in the plasma and 1 micro molar in the reticulum.



$$\Delta G = nRT \ln \frac{C_{ret}}{C_{plas}} + (0.5)Z\mathcal{F}(\phi_{ret} - \phi_{plas})$$

$$= (0.5)(8.3145)(298)\ln\left(\frac{1\times10^{-6}}{1\times10^{-9}}\right) + 0.5(2)(96500)(0.060)$$

$$= +8560\ J + 5790\ J$$

$$\Delta G = \boxed{14350\ J}$$

(b) What is the change in chemical potential for Ca^{+2} for the process in (a)?

$$\Delta\mu = \frac{\Delta G(J)}{n\ (mol)} = \frac{+14350}{0.5}\frac{J}{mol} = \boxed{28700\ J/mol}$$

(20 pts) **9.** The atmospheric pressure in Bozeman = 0.83 and the boiling point of pure water in Bozeman is 93 °C. ← 366 K

(a) What is K (the equilibrium constant) for the evaporation reaction at 93° C

H_2O (liquid) --> H_2O(gas) ?

$(P_{H_2O})_{eq}$ = atmospheric = 0.83 is vapor pressure at 93°C

at 93°C $K = \dfrac{(P_{H_2O})_{eq}}{X_{H_2O(\ell)}} = \dfrac{0.83}{1} = 0.83$

(b) At what temperature will a salt solution with $a_{H2O(\ell)} = 0.80$ boil in Bozeman? (ΔH^0_{vap} = 40.7 kJ/mol)?

$K_{T_{boil}} = \dfrac{0.83\ atm}{0.80} = 1.0375$

$K = \dfrac{P_{H_2O(g)}}{a_{H_2O(\ell)}} =$

$\ln \dfrac{K_2}{K_{366}} = -\dfrac{\Delta H^0}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right) = -\dfrac{40700}{8.3145}\left(\dfrac{1}{T_2} - \dfrac{1}{366}\right)$

$\ln \dfrac{1.038}{0.83} = -\dfrac{40700}{8.3145}\left(\dfrac{1}{T_b} - \dfrac{1}{366}\right)$

$\dfrac{1}{T_b} = -\dfrac{8.3145}{40700}\ln\left(\dfrac{1.038}{0.83}\right)_s + \dfrac{1}{366} = 0.002686$ $\quad T_b = 372\ K$

(20 pts) **4.** If a Henry's Law constant for a gas in water = 100 atm/M at 350 K and is 50 atm/M ~~M/atm~~ at 300 K, what is ΔH^0 for the ***evaporation*** of the gas fro

$$gas(aq) \longrightarrow gas(g) \quad K =$$

$$\ln \frac{K_{350}}{K_{300}} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{350} - \frac{1}{300}\right) = \ln \frac{100}{50}$$

$$\Delta H^\circ = \frac{-R \ln\left(\frac{K_2}{K_1}\right)}{(350^{-1} - 300^{-1})} = \frac{-(8.3145)\ln 2}{-0.000476} = 12110 \text{ J}$$

(20 pts) 3. (a) If the terminal velocity of a molecule under a typical ultracentrifuge force of 1 x 10^{-11} g cm s^{-2} at 300 K is 2 x 10 -5 cm/s what is its effective frictional coefficient?

$u_{Term} = \frac{Force}{f}$ $\quad f = \frac{Force}{u} = \frac{1 \times 10^{-11}\ g\ cm\ s^{-2}}{2 \times 10^{-5}\ cm\ s^{-1}}$

$= 0.5 \times 10^{-6} = \boxed{5 \times 10^{-7}\ g\ s^{-1}}$

(b) What is its diffusion coefficient?

$D = \frac{K_B T}{f} = \frac{1.38 \times 10^{-16}\ g\ cm^2\ s^{-2} \times 300\ K}{5 \times 10^{-7}\ g\ s^{-1}}$

$= \boxed{8.3 \times 10^{-8}\ \frac{cm^2}{s}}$ or $8.3 \times 10^{-12}\ \frac{m^2}{s}$

2

(10 pts) 7. (a) For the amino acid tyrosine, indicate the fraction protonated and the average charge of each residue at pH 7, accurate to within 0.1 charge unit. What will be the **total charge** on the amino acid when pH 7?

Amino acid	**Ka**	**Charge when protonated**	**Fraction Protonated**	**Ave. Charge**
Histidine side chain	$1x10^{-6}$	+1	0.1	+ 0.1
Amino group	$1x10^{-9}$	+1	0.99	+ 1
Carboxylate group	$1x10^{-3}$	0	10^{-4}	

Total charge = + .1

Stoichiometric: $A + B \rightarrow C$

(20 pts) **3.** **(a)** If a molecule A disappears by at a rate that is directly proportional to the amount of A present, what is the rate law [redacted] disappearance of A is 0.001 grams/second when 10 grams of A is present?

therefore is 1st order in A

$$\text{rate} = -\frac{d m_A}{dt} = K m_A$$

$$= 0.001\ g\ s^{-1} = K\ 10\ g$$

$$K = \frac{0.001\ g\ s^{-1}}{10\ g} = 1 \times 10^{-4}\ s^{-1}$$

(b) Write a simple plausible mechanism for this reaction. (There are many correct answers, but all will have one thing in common.)

$A \rightarrow X$ slow (rate determining step)

$X + B \rightarrow C$ fast

Sum $A + B \rightarrow C$

(12 pts) **3.** For the reaction A + B --> C + D, the rate law was measured to be -d[A]/dt = k [A][B] and the following mechanism was proposed.

1) $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X$ — rate = $k_1[A][B]$

2) $X \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Y$

3) $Y \xrightarrow{k_3} C + D$

There are 3 choices as to which of the 3 steps is rate determining.

Is it possible to determine which of the three choices is the true rate determining step. For full credit you will need to demonstrate why your answer is correct.

if 1) is R.D.S. $rate_1 = k_1[A][B]$

if 2) is RDS $rate_2 = k_2[X]$ 1) at equil.

but $k_1[X] = k_1[A][B]$ $[X] = \frac{k_1}{k_{-1}}[A][B]$

so $rate_2 = k_2 \frac{k_1}{k_{-1}}[A][B]$

if (3) is RDS $rate_3 = k_3[Y]$, but $k_{-2}[Y] = k_2[X]$

$rate = k_3 \cdot k_2[X] = k_3 \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}}[A][B]$

ALL 3 cases give rate $\propto [A][B]$

CANNOT DISTINGUISH.

(20 pts) 5. (a) If 10% of the infra-red light emitted by the ground at a certain frequency is ***absorbed*** by CO_2 on its way from the ground to an elevation of 1 km, what fraction will be ***absorbed*** after it travels to an elevation of 20 km?

$T = 1 - \text{fraction absorbed}$

$= 1 - 0.1 = 0.90$

$A_{1km} = -\log(0.90) = 0.0458$

$A = \epsilon c \ell$

$A_{20\,km} = 20\, A_{1\,km} = 0.915$

$T_{20\,km} = 10^{-A} = 10^{-0.915} = \boxed{0.121}$

(20 pts) **2.** From $dH = TdS + VdP$ $= \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S$

a) $\left(\frac{\partial H}{\partial S}\right)_P = T$

b) $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

(15 pts) **8.** Explain in a brief paragraph why it is that the sky appears blue whereas the light at sunset is red.

9. In a short paragraph, describe the physical basis for magnetic resonance imaging, making it clear how it is possible to get an image, and comparing to NMR.

TABLE A.1 Useful Physical Constants

		SI units	cgs-esu units
Gas constant	R	8.3145 J K^{-1} mol^{-1}	8.3145×10^7 erg deg^{-1} mol^{-1} 1.987 cal deg^{-1} mol^{-1} 0.08205 L atm deg^{-1} mol^{-1}
Avogadro's number	N_0	6.0221×10^{23} mol^{-1}	6.0221×10^{23} molecules mol^{-1}
Boltzmann constant	k	1.3807×10^{-23} J K^{-1}	1.3807×10^{-16} erg deg^{-1}
Faraday constant	F	9.6485×10^4 C mol^{-1}	9.6485×10^4 C mol^{-1}
Speed of light	c	2.9979×10^8 m s^{-1}	2.9979×10^{10} cm s^{-1}
Planck constant	h	6.6261×10^{-34} J s	6.6261×10^{-27} erg s
Elementary charge	e	1.6022×10^{-19} C	4.8030×10^{-10} esu
Electron mass	m_e	9.1094×10^{-31} kg	9.1094×10^{-28} g
Proton mass	m_p	1.6726×10^{-27} kg	1.6726×10^{-24} g
Standard gravity	g	9.8066 m s^{-2}	980.66 cm s^{-2}
Permittivity of vacuum	ε_0	8.8542×10^{-12} C^2 N^{-1} m^{-2}	

C = coulomb, g = gram, J = joule, K = Kelvin, kg = kilogram, L = liter, m = meter, N = newton, s = second

TABLE A.5 Inorganic Compounds*

	$\Delta H_f^0 \equiv \bar{H}^0$ (kJ mol^{-1})	$\bar{S}^0$ (J K^{-1} mol^{-1})	$\Delta G_f^0 \equiv \bar{G}^0$ (kJ mol^{-1})
Ag(s)	0	42.55	0
$Ag^-(aq)$†	105.579	72.68	77.107
AgCl(s)	−127.068	96.2	−109.789
C(g)	716.682	158.096	671.257
C(s, graphite)	0	5.740	0
C(s, diamond)	1.895	2.377	2.900
Ca(s)	0	41.42	0
$CaCO_3$(s, calcite)	−1206.92	92.9	−1128.79
$Cl_2(g)$	0	223.066	0
$Cl^-(aq)$	−167.159	56.5	−131.228
CO(g)	−110.525	197.674	−137.168
$CO_2(g)$	−393.509	213.74	−394.359
$CO_2(aq)$	−413.80	117.6	−385.98
$HCO_3^-(aq)$	−691.99	91.2	−586.77
$CO_3^{2-}(aq)$	−677.14	−56.9	−527.81
Fe(s)	0	27.28	0
$Fe_2O_3(s)$	−824.2	87.40	−742.2
$H_2(g)$	0	130.684	0
$H_2O(g)$	−241.818	188.825	−228.572
$H_2O(l)$	−285.830	69.91	−237.129
$H^+(aq)$	0	0	0
$OH^-(aq)$	−229.994	−10.75	−157.244
$H_2O_2(aq)$	−191.17	143.9	−134.03
$H_2S(g)$	−20.63	205.79	−33.56
$N_2(g)$	0	191.61	0
$NH_3(g)$	−46.11	192.45	−16.45
$NH_3(aq)$	−80.29	111.3	−26.50
$NH_4^+(aq)$	−132.51	113.4	−79.31
NO(g)	90.25	210.761	86.55
$NO_2(g)$	33.18	240.06	51.31
$NO_3^-(aq)$	−205.0	146.4	−108.74
$Na^+(aq)$	−240.12	59.0	−261.905
NaCl(s)	−411.153	72.13	−384.138
NaCl(aq)	−407.27	115.5	−393.133
NaOH(s)	−425.609	64.455	−379.494
$O_2(g)$	0	205.138	0
$O_3(g)$	142.7	238.93	163.2
S(rhombic)	0	31.80	0
$SO_2(g)$	−296.830	248.22	−300.194
$SO_3(g)$	−395.72	256.76	−371.06